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Lattice Parameters and Debye Temperature of $Nacl_x$ $Nabr_{y-X}$ Kcl_{1-Y} Ternary Mixed Crystals

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Abstract: *Mixed crystals of alkali halides find applications in optical, optoelectronics and electronic devices. In the present study the pure and mixed crystals of $NaCl_x$ $NaBr_{y-x}$ KCl_{1-y} were grown from the aqueous solution. The grown crystals were characterized by taking XRD, TG/DTA and Vicker's hardness measurement. The Debye temperature is an important parameter of a solid. Several methods of evaluating Debye temperature are available. In the present study Debye temperature were calculated from the Debye- Waller factor, melting point and microhardness. The results were compared with the Kopp-Neumann relation.*
Keywords: *Mixed crystals, Alkali halides, Debye temperature*

I. Introduction

The Debye temperature is an important parameter of a solid. Several methods of evaluating the Debye temperature are available. Alers (1965) reviewed number of these. The present paper deals with four different methods of calculating Debye temperature. The methods considered here are a) from melting point b) from Debye-Waller factor c) from microhardness d) from Kopp-Neumann relation. The comparison of the results by the first three methods with those the last one enables one to judge the accuracy of the various methods.

Single crystals of pure and binary, ternary and quartnery mixed crystals alkali halides have been grown for a very long time. So in the present study we grow pure and ternary mixed crystals of NaCl NaBr and KCl. The mixed crystals of alkali halides are found to be harder than the end members and so they are more useful in several applications in optical, optoelectronic and electronic devices. Sirdeshmukh et.al [1] reported that impurity hardening is more effective than solid solution hardening. So in the present study we grow the pure and ternary mixed crystals of NaCl NaBr and KCl.

II. Experimental details

2.1.Growth of sample crystals

Analytical Reagent (AR) grade NaCl NaBr and KCl substances and doubly distilled water were used in the present investigation. An aqueous solution of the salt with desired molecular ratio was prepared at supersaturated concentration. The temperature and volume were kept constant respectively at 32^{o}C and 100ml for all the crystals.

In the present study total of ten crystals (three end members seven mixed crystals) for various values of x and y were grown in identical conditions.

2.2.Estimation of bulk composition

The compositions of pure and mixed crystals were accurately estimated from EDAX spectrum taken by SUTW-SAPPIRE DIRECTOR OF 1339.91 RESOLUTION.

2.3.Debye temperature calculation

Debye temperature of the crystals can be determined from various experimental measurements like melting point, Debye- Waller factor, hardness number, Kopp-Neumann relation etc.

2.3.1.Mellting point

Debye temperature can be estimated from the melting point(Tm) of the crystal using the formula [2]

$$\theta_m = C[Tm/MV^{2/3}]^{1/2}$$

where C is a constant depending on the structure. The unit volume was estimated from the lattice constant. A value of 192.43 has been used for C as the structure of NaCl type. This value evaluated from the known values of Debye temperature for the end member crystals. The melting point of all the grown crystals were determined from TG/DTA curve recorded on SEIKO TGDTA 6200 system at heating rate of 10^{o}C /min. Nitrogen was used as purge gas at a flow rate of 500ml/min.

2.3.2. Debye-Waller factor

The mean Debye- Waller factor was determined from the XRD data taken by using PAN analytical diffractometer with CuKα(=1.5406Å) radiation. The reflections were indexed following the procedures of Lipson and Steeple [3]. Analysis of the X-ray diffraction peaks by the available methods [4] shows that for the mixed crystals, all the X-ray diffraction peaks can be indexed with single fcc phase.

The mean Debye- Waller factor for all the ten grown crystals was determined by a method similar to that followed by Mahadevan and his co-workers[2,5-11]. As the number of reflections are limited, only a common Debye- Waller factor was determined for all the atoms in every system by Wilson theory [12].

The scattering factors were calculated using the relations

$F_{(hkl)} = 4(f_{Na+} \pm f_{Cl-})$ for NaCl

$F_{(hkl)} = 4(f_{Na+} \pm f_{Br-})$ for NaBr

$F_{(hkl)} = 4(f_{K+} \pm f_{Cl-})$ for KCl

$F_{(hkl)} = 4(x(f_{Na+} \pm f_{Cl-})+(y-x)(f_{Na+} \pm f_{Br-})+(1-y)(fK_{+} \pm f_{Br-}))$ for the mixed systems.

Here f_{Na+},f_{K+}, f_{Br-} and f_{Cl-} are the respective scattering factors for Na^+, K^+, Br^- and Cl^- ions, calculated from the nine parameters taken from the literature[13] x,(y-x) and (1-y) are the compositions of NaCl NaBr and KCl present in the mixed system. The plus sign for the reflections with even values of h+k+l and minus sign for those with odd values of h+k+l.

The equation for Bragg intensity may be written in logarithmic scale as

$$(I_E/I_c) = K\exp(-2B\sin^2\theta/\lambda^2)$$

The mean Debye- Waller factor (Bobs) was obtained by taking a least squares approximation of ln (I_E/I_c) against $\sin^2\theta/\lambda^2$. I_E is experimental observed (integrated) intensity, I_C is the wavelength of radiation used.

The presence of mixing of ions creates a static contribution in the case of mixed crystals. In the present study among the four ions viz Na^+, K^+, Br^- and Cl^- ions, replacement is possible between Cl^- and Br^-

$$B_{static} = x(1-y)(r_A-r_B)^2+x(y-x)(1-y)(r_C-r_D)^2$$

where x,(1-y) and (y-x) are respective mole fractions of NaCl,NaBr and KCl. In the mixed crystals r_A,r_B, r_C,r_D are the respective ionic radii of NaCl,NaBr and KCl.

Observed Debye –Waller factors for the mixed crystals is given by

$$B_{observed} = B_{static}+B_{thermal}$$

$B_{thermal}$ was calculated from the above relation and the Debye temperature was determined from the methods followed by Neelakanda Pillai and Mahadevan[2].

The Debye temperature (θ_D) was obtained from the Debye – Waller theory expressions.

For pure crystals

$$B_{obs} = (6h^2/mkT)\,W(x)$$

$$B_{thermal} = (6h^2/mkT)W(x)$$

Where m is the mean atomic mass, T is the absolute temperature (298K) at which the X-ray diffraction intensities were measured, h is the Planck's constant and k is the Boltzmann's constant.

The function W(x) is given by

$$W(x) = (\varphi(x)/x^2)+(1/4)x$$

Where $x= \theta_D/T$ and φ(x) is an intergral

$$\varphi(x) = \int_0^{\infty} (e^y/1-e^y)dy$$

the value of W(x) for a wide range of x are calculated by Benson and Gill[14], θ_D the Debye temperature was evaluated by using the above expression.

2.3.3 Microhardness value

Debye temperature can also be estimated from the microhardness value calculated from Vicker's microhardness using the relation

$$\theta_D = BH^{1/2}V^{1/6}M^{-1/2}$$

Where B is a constant and its value is 100, which is calculated from the known KCl data.

2.3.4 Kopp-Neumann Relation

Sirdeshmukh and Srinivas[16] reviewed the data on fourteen alkali halide mixed crystals and conducted that, by and large,the composition dependence of θ_D (ie.θ) of alkali halide mixed crystals is well described by the Kopp-Neumann relation given by

$$\theta^{-3} = x\,\theta_A^{-3}+y\,\theta_B^{-3}+z\,\theta_C^{-3}$$

where θ_A, θ_B and θ_C are the Debye temperature of the end member crystals.

III. Results and Discussion

3.1. Growth

All the crystals grown in the present study are shown in the figure 1. The grown crystals are stable, transparent and good quality.

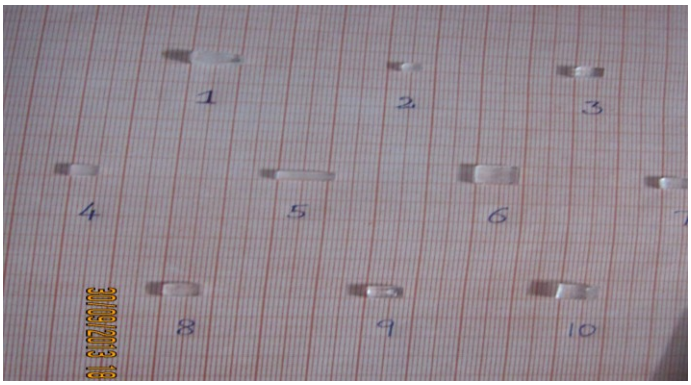

Figure 1 Photographs of grown crystals

3.2.Estimation of Bulk Composition

The compositon of all the ctystal were estimated from the EDAX data . EDAX spectrum of $NaCl._5$ $NaBr._3KCl._2$ is provided in fig2

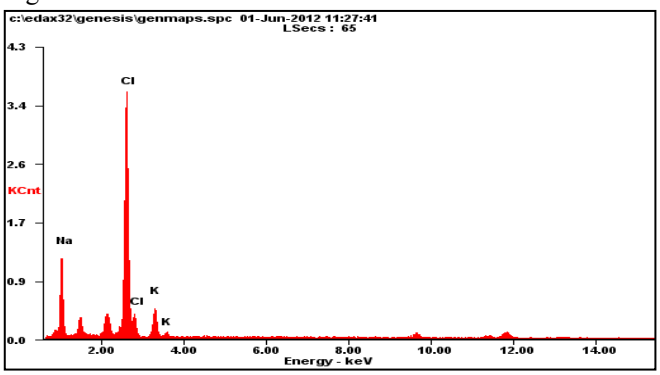

Fig2 EDAX spectrum of $NaCl._5$ $NaBr._3KCl$

The weight percentage of all the atoms present in the crystal along with estimated composition is given in table 1. It is found that the estimated composition will agree with the actual composition taken.

Table I Estimated composition from EDAX

System	Weight percentage of				Estimated composition		
	Na	K	Cl	Br			
$NaCl._2$, $NaBr._4KCl._4$	29.14	8.21	51.70	10.88	0.169	0.441	0.390
$NaCl._3$, $NaBr._3KCl._4$	10.46	10.08	61.95	17.52	0.330	0.307	0.362
$NaCl._5$, $NaBr._1KCl._4$	1.68	47.85	38.70	11.76	0.504	0.107	0.392
$NaCl._4$, $NaBr._4KCl._2$	39.85	30.4	22.43	7.28	0.39	0.402	0.189
$NaCl._5$, $NaBr._3KCl._2$	33.81	27.28	33.76	5.06	0.489	0.304	0.191
$NaCl._6$, $NaBr._2KCl._2$	37.91	38.64	18.23	5.22	0.537	0.189	0.232
$NaCl._7$, $NaBr._1KCl._2$	36.54	17.78	37.79	3.03	0.607	0.107	0.188

3.3. Lattice parameter

The observed lattice parameters of all the crystals grown are given in table 2. Along with these calculated from Vegard's law and Retger's rule. XRD pattern of $NaCl._5$ $NaBr._3KCl._2$ is shown in fig 3for illustration. It is found that the observed lattice parameters of the end members agreed with the reported value[17] and all the Xray diffraction peaks could be indexed with single fcc phase. According to Tobolski[15] two or three alkali halide will form continous solid solutions provide the difference between their lattice parameter is less than 6%. Here, the percentage difference in lattice parameter between KCl and NaBr is4.8%. Also, the percentage difference between NaBr and NaCl is 5.98%. So, complete miscibility is expected. Observation of single fcc phase for all the mixed crystals in the present study is in line with this. It is also seen that the observed values there was a slight deviation from Vegard's law and Retger's rule.

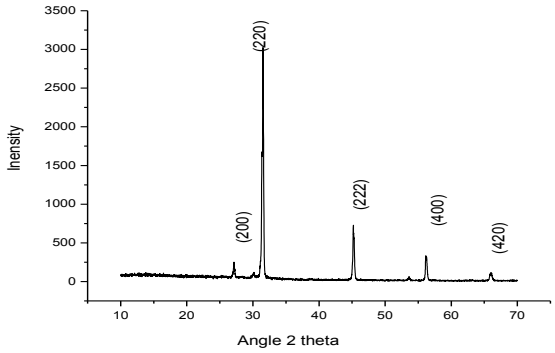

Figure 3 XRD pattern of $NaCl._5$, $NaBr._3KCl._2$

Table 2 The observed Lattice Parameters from Vegard's law and Retger's rule for pure and mixed crystals

System	Lattice parameters		
	a	Vegard's law	Retger's rule
NaCl	5.6664		
NaBr	5.977		
KCl	6.3114		
$NaCl._2$, $NaBr._4KCl._4$	6.4876	6.0858	6.090
$NaCl._3$, $NaBr._3KCl._4$	5.6604	6.0672	6.0811
$NaCl._5$, $NaBr._1KCl._4$	5.67143	6.0787	6.0889
$NaCl._4$, $NaBr._4KCl._2$	5.6714	6.0290	6.034
$NaCl._5$, $NaBr._3KCl._2$	5.6582	6.0144	6.0338
$NaCl._6$, $NaBr._2KCl._2$	5.6465	6.0335	6.0542
$NaCl._7$, $NaBr._1KCl._2$	5.6513	6.0344	6.0578

3.4. Debye Temperature

The thermal parameters obtained in the present study viz.Debye-Waller factor ($B_{observed}$,B_{static} and $B_{thermal}$) and Debye temperature.

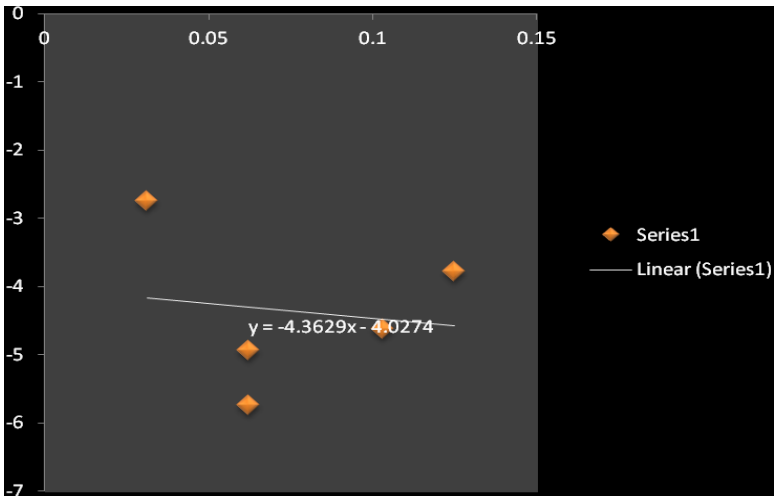

Fig.4.Wilson plot of the sample $NaCl._5$ $NaBr._3KCl._2$

The reported values of Debye- waller factors and Debye temperature for the end member crystals are provided in bracket. The Debye temperature determined from the Debye – waller factor of mixed crystals show a non-linear variation with composition. The Debye temperature calculated from the melting point microhardness and from Debye-Waller factor are provided in table 3 along with those calculated from Kopp-Neumann relation. It is found that the Debye temperature calculated from the melting point and microhardness the Debye-Waller factor for y=0.6 coincide with the estimated value from the Kopp-Neumann relation. But in the case of y=0.8 it is higher than the values estimated from the Kopp-Neumann relation.In all the three experimental methods it varies non-linearly with composition. The non-linear variation of Debye temperature with composition may due to the increase in the vibrational entropy due to mixing.

Table :3 Debye temperatures calculated from the melting point,microhardness,Debye- Waller and Kopp-Neumann relation along with system.

System	Debye temperature						
	Debye -Waller factor		Melting point ° (K)		Microhardness		Kopp-Neumann
	$B_{thermal}$	θ_D	Melting Point values	θ_D	Hardness values	θ_D	
NaCl	-	275	1078.2	145.6	20.5	139.86	
NaBr	-	202	1020	101.36	21.38	110.74	
KCl	-	154	1046.7	114.24	16.38	117.72	
$NaCl_{.2}$, $NaBr_{.4}KCl_{.4}$	6.54	148.77	1026.7	116.73	13.2	113.35	160.58
$NaCl_{.3}$, $NaBr_{.3}KCl_{.4}$	2.05	117.185	1010	137.89	15.1	122.17	150.17
$NaCl_{.5}$, $NaBr_{.1}KCl_{.4}$	-33.91	126.94	1039	161.25	23	168.11	190.78
$NaCl_{.4}$, $NaBr_{.4}KCl_{.2}$	6.67	123	1037.5	144.33	11.7	107.63	151.40
$NaCl_{.5}$, $NaBr_{.3}KCl_{.2}$	-11.94	245.25	1041	153.05	11.9	114.57	145.58
$NaCl_{.6}$, $NaBr_{.2}KCl_{.2}$	-31.56	229.311	1043.5	160.87	11.7	118.88	138.1
$NaCl_{.7}$, $NaBr_{.1}KCl_{.2}$	-63.41	248.085	1048.7	169.53	12.1	127.15	141.0

IV. Conclusion

The mixed crystals $NaCl_x$ $NaBr_{y-x}$ KCl_{1-y} were grown from the aqueous olution. The lattice parameters calculated from the X-ray diffraction data show that the system exhibits only a single fcc phase and the lattice parameters almost obey the Regard's law. The Debye temperature determined from the melting point, Debye – Waller factor and microhardness show non-linear variation with composition may due to the increase in the vibrational entropy due to mixing.

References

[1]. D.B.Sirdeshmukh, T. Kumarasway, P.Geetakrishna, K.G.Subhadra, Bull mater. Sci, 26 (2003)261-265
[2]. N.Neelakandapillai, C.K.Mahadevan, physica, 463, 2168 (2008).
[3]. H.Lipson, H.Steeple, Interpretation of X-ray powder diffraction patterns, Macmillan Newyork, 1970.
[4]. B.E.Warren, X-ray diffraction, Addison Wesley California 1969.
[5]. K.Jeyakumari, C.Mahadevan, J.Phy.Chem Soil 66(2005)1705.
[6]. S.Perumal, C.K.Mahadevan, Physica B 367(2005) 172
[7]. S.Perumal, C.K.Mahadevan, Physica B 369(2005) 172
[8]. G.Selvarajan, C.K.Mahadevan, J.Mater Sci, 41(2006)8211
[9]. G.Selvarajan, C.K.Mahadevan, J.Mater Sci, 41(2006)8218
[10]. C.M.PadmaC.K.Mahadevan, Mater Manuf Processes
[11]. M.Priya and C.K.Mahadevan, PhysicaB (2007)10, 1016.
[12]. A.J.C.Wilson, Nature 150(1942) 151.
[13]. D.T.Cromer, J.B.Mann, ActaCrystalloger A24(1968)321.
[14]. G.C.Benson, E.K.Gill, table of integral functions related to Debye-Waller factor, National Research Council of Canada, Ottawa 1966.
[15]. A,V.Toholsky, K. Chem. Phys.31. 1526, 1959.
[16]. D.B.Sirdeshmukh, K.Sriniwas, J.Mater.Sci 21(1968).
[17]. D.B.Sirdeshmukh, l.sirdeshmukh and K.G.Subhdra (2001), Alkali halides- A hand book of physical properties (Springer,Berlin)